MODELING FRAMEWORK DESIGN
HOUSATONIC RIVER MODELING PEER REVIEW

DRAFT REPORT

INTRODUCTION

I should begin by saying that I was impressed by the Modeling Framework Design (MFD) report and the associated Quality Assurance Project Plan (QAPP). These documents address a complex problem, in terms of the modeling objectives, and largely succeed in developing a defensible modeling approach. Complexities of the site and of the aquatic and terrestrial ecosystem, along with numerous uncertainties, data limitations, and other constraints, makes the Housatonic River PCB contamination as difficult a problem as I have seen. It has required substantial effort to absorb and understand all of the elements of the MFD. With each reading (and re-reading) of the various report sections, my understanding of the proposed modeling approach has changed. A more open dialogue amongst the peer reviewers, and between the panel and the modeling team, would have greatly facilitated this process.

I would also like to say that, to some extent, the value of peer review at this stage of the project is fairly limited. There are two reasons for this. First, you hire a modeler, not a model. By that I mean the choice of model and modeling approach depends upon who is doing the modeling. We have all invested years of effort developing expertise in at most a handful of models, gaining skill in their use through site-specific applications. The choice of models and modeling approaches that comprise the MFD are essentially complete once the modeling team is selected, and this bridge has been crossed. The reaction of the modeling team to the questions posed on March 22 bears this out.

Secondly, it can be difficult to judge the success of modeling based upon prior review. The success of modeling is judged in terms of predictions, not formulations. At best, we can compare the overall MFD and it's elements to models and modeling approaches which have succeeded or failed in the past. However, it is possible that alternative models and approaches may perform as well (or better). I have struggled with this issue through much of the MFD, particularly with aspects of the MFD considered ***avante garde*** by the standards of most water quality modelers. These include:

- the prediction of PCB loads via the HSPF watershed model,
- the incorporation of the food web bioaccumulation simulation within an ecosystem model,
- kinetic models of PCB partitioning to detrital and planktonic organic carbon, and
- the direct use of SEDFLUME experimental data to parameterize sediment resuspension properties.

The defense of the avante garde is made by the modeling team:

> New applications and linkages of existing models are not necessarily undesirable. Development of a successful modeling framework for a challenging problem such as the evaluation of baseline conditions and alternative PCB remediation strategies for the Housatonic River has the potential to significantly advance the body of knowledge for contaminant transport and fate modeling in riverine systems.[1]

However, there are risks which accompany innovation; most obviously, the risk of failure. Prior success may be the best indicator of a favorable outcome. This conservative philosophy is one basis of the engineering discipline. Many of the comments submitted by Quantitative Environmental Analysis (QEA) on November 30, 2000 critical of the MFD are a reflection of the conservatism. A second risk is that if too much effort is devoted to making a new application succeed, some other more fundamental task may be overlooked or shortchanged, possibly jeopardizing the project. The tolerance for risk is much higher in the research and development environment than it is in the regulatory arena. Since the stated objectives of this project fall entirely within the latter, it is necessary to consider the "What if this doesn't work?" contingency in the event of failure. I have concluded that constructive criticism of the avante garde approach can best take the form of suggesting what additional data collection, analytical and modeling efforts are appropriate as contingencies. Contingency plans need to be built into the MFD.

This review report is organized in two sections. In the first, some fairly brief responses to the Charge For The Hydrodynamic Modeling Peer Review (Objectives of Modeling Approach, Summary of Charge, and Peer Review Questions) are offered. These need further development. The second section offers more specific comments on the MFD and the Modeling QAPP. Where possible, I have cross-referenced specific comments to their relevance in terms of the Peer Review Charge. Following the Public Meeting next week, I intend to merge the sections together into a more coherent document.

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[1] Text in red is from *EPA Response to Peer Review Panelist Questions on the Housatonic River Modeling Framework Design* (April 12, 2001).

I. RESPONSE TO CHARGE FOR THE HYDRODYNAMIC MODELING PEER REVIEW

Objectives Of Modeling Approach

There are numerous objectives for the modeling effort which are summarized below:

- **Quantify future spatial and temporal distribution of PCBs (both dissolved and particulate forms) within the water column and bed sediment;**

- **Quantify the historical and current relative contributions of various PCB sources to PCB concentrations in water and bed sediment;**

The MFD does not address how HSPF will predict past PCB loadings for long-term confirmation (hindcast) simulations.

- **Quantify the historical and current relative contribution of various PCB sources to bioaccumulation in target species.**

- **Estimate the time required for PCB-laden sediment to be effectively sequestered by the deposition of uncontaminated material (i.e. natural recovery).**

- **Estimate the time required for PCB concentrations in fish tissue to be reduced to levels established during the risk assessment process, that no longer pose either a human health or ecological risk, based upon various response and restoration scenarios;**

The MFD does not address how remedial action in the Rest-of-River study area will be represented in the different models.

- **Quantify the relative risk(s) of extreme storm event(s) contributing to the resuspension of sequestered sediment or the redistribution of PCB-laden sediment in the study area.**

Summary of Charge

The Peer Review Panel will be convened to review the modeling exercise (including the hydrodynamics component, the sediment transport component, the PCB fate and transport component, and the bioaccumulation component) at a minimum of three intervals during the modeling process: model construction, calibration, and validation. The Peer Review Panel shall focus on the following general issues (more specific questions are identified below):

- **Do the modeling frameworks include the significant processes, and are the descriptions of those processes sufficiently accurate to represent the hydrodynamics, sediment transport, and the chemistry, fate and transport, and bioaccumulation of PCBs in the Housatonic River?**

The accuracy of watershed PCB loadings predicted by HSPF may be inadequate to achieve goals for accuracy in other model predictions of PCB concentrations in water, sediment, and biota.
Sediment/sorbent transport (state variable linkages) may not be sufficiently accurate.
PCB partitioning should be based on equilibrium with dissolved and particulate organic carbon phases.
Bioaccumulation model would preferably simulate age classes for all fish species (instead of just one).

- **Are the available data sufficient for development of models of the hydrodynamics, sediment transport and the chemistry, fate and transport, and bioaccumulation of PCBs in the Housatonic River?**

Data are lacking for:

Tributary boundary conditions
Bed load of sediment and PCBs
Erosion Rates (including aggrading bars/terraces and banks)
PCB partitioning
Lower food web PCB concentrations
Diet (predator/prey relationships)

- **Are the processes in the final models calibrated/validated to the extent necessary for prediction of future conditions?**

Accuracy of both event and long-term simulations may be difficult to demonstrate due to lack of necessary validation data ("big event" sampling and data quality and comparability issues re long-term contaminant decline).

Without additional data identified above, significant model processes will not be adequately constrained by calibration to ensure reliability of forecast predictions.

- **How sensitive are the models to uncertainties in the descriptions of the relevant processes?**

In terms of PCBs predicted in water and sediment, the most significant uncertainties are associated with the following processes:

Loadings (PCBs and sediments)
Initial conditions for sediment PCB concentrations
Resuspension and deposition fluxes (especially at high shear stresses)
Sediment bed mixing and diffusion
Partition coefficients

For PCB concentrations predicted in fish, additional uncertainties include:

Plankton and benthos biaccumulation
Fish prey, dietary contaminant assimilation relative to food, and elimination rates

Peer Review Questions

In considering the foregoing general issues and evaluating the EPA documents, the Peer Review Panel shall give specific consideration to the following questions. As modeling activities proceed, additional specific questions may be identified the panel to address.

Modeling Framework and Data Needs

1. Do the modeling frameworks used by EPA include the significant processes affecting PCB fate, transport, and bioaccumulation in the Housatonic River; and are the descriptions of these processes in the modeling framework(s) sufficiently accurate to represent the hydrodynamics, sediment transport, PCB fate and transport, and PCB bioaccumulation in the Housatonic River?

In general, the MFD does identify the significant processes affecting PCB fate, transport, and bioaccumulation in the Housatonic River. The process descriptions are also generally adequate; as mentioned, some of the process models are avant garde. Weaknesses in the process descriptions are discussed in Section II for:

- *Food web predator/prey linkages and feeding descriptions at the base of the food web,*
- *Surficial sediment mixing,*
- *Chemical transport and fate descriptions in EFDC, and*
- *Some alternatives are offered to the organism-level bioaccumulation formulations*

and parameterization used in AQUATOX,
- *Detrital carbon sorption kinetics model used in AQUATOX.*

There also appear to be substantial issues to address with respect to the sediment resuspension and deposition processes. However, I will leave this to other Peer Reviewers who know a lot more about sediment transport.

I would suggest discarding "Non-partitioning of PCBs" and wind-driven transport processes from conceptual model.

2. Based upon the technical judgment of the Peer Review Panel:

a. Are the modeling approaches suitable for representing the relevant external force functions (e.g.. hydraulic flows, solids and PCB loads, initial sediment conditions, etc.), describing quantitative relationships among those functions, and developing quantitative relationships between those functions and PCB concentrations in environmental media (e.g., water column, sediments, fish and other biota, etc.)?

- *Complete and accurate loadings of solids, organic carbon, and especially PCBs is probably the most critical factor in the success of the mass balance models;*
- *HSPF is not suitable (unless confirmed) for prediction of PCB nonpoint loadings;*

b. Are the models adequate for describing the interactions between the floodplains and the river?

It is unclear whether the proposed linkage will correctly predict the net transport of PCBs from the river to the flood plain. Hopefully, issues with this approach can be discussed at the Public Meeting.

c. Are the models adequate for describing the impacts of rare flood events?

Other models have been demonstrated to accurately describe sediment transport impacts of flood events (excluding bank slumping and small-scale bed features). However, model adequacy must be demonstrated in each system due to great variability. Not sure that magnitude of sampled "flow events" is large enough for such demonstration. Unclear whether impacts of rare flood events on PCB transport, fate, and bioaccumulation can be demonstrated conclusively (data limitations).

d. Are the models adequate for discriminating between water-related and sediment-related sources of PCBs to fish and other biota?

The question is poorly posed. Food web bioaccumulation models <u>*can*</u> *simulate PCB accumulation via sediment and water exposure routes, given appropriate information regarding diet.*

3. Again, based upon the technical judgment of the Panel, are the spatial and temporal scales of the modeling approaches adequate to address the principal need for the model - producing sufficiently accurate predictions of the time to attain particular PCB concentrations in environmental media under various scenarios (including natural recovery and different potential active remedial options) to support remedial decision-making in the context described above in the Background section? If not, what levels of spatial and temporal resolutions are required to meet this need?

Upstream spatial domain of transport and fate model is an issue here.
Spatial/temporal resolution of AQUATOX appears adequate for simulating PC bioaccumulation, although greater resolution of spatial variability in PCB sediment concentrations would be desirable.
EFDC spatial resolution is not defined; should be related to variability of sediment bulk and erosion properties, PCB concentrations, and appropriate scale for resolving bed loads.
Methodology for establishing initial sediment PCB concentrations (at 2 resolutions and for both 1979 and 1999) not defined. Similarly, the design of simulations for remediation scenarios is not addressed, especially for the case of remedial action altering sediment PCB concentrations at spatial scales substantially smaller than model spatial resolutions.

4. Is the level of theoretical rigor of the equations used to describe the various processes affecting PCB fate and transport, such as settling, resuspension, volatilization, biological activity, partitioning, etc., adequate, in your professional judgment, to address the principal need for the model (as defined above)? If not, what processes and what resolution are required?

There are various process representations for PCB transport and fate, which vary in terms of complexity and theoretical rigor. However, most models have adopted representations which are consistent with well-accepted principles: organic carbon-based equilibrium partitioning in both particulate and dissolved phases, two-film resistance volatization using temperature-dependent Henry's constants, a well-mixed surficial sediment layer, reductive dehalogenation of specific congeners above a saturation concentration, and molecular diffusion from pore water. Assumptions of equilibrium partitioning when applied to PCB desorption from resuspended sediments is a potentially significant weakness of most models.

Models of PCB transport and fate, and underlying theory, are not sufficiently robust that parameter values determined a priori can account for all of the site-specific variability that is observed in critical model parameters. This is not a weakness of the models specifically, rather an acknowledgment that all transport and fate models are imperfect representations of chemical behavior in an extremely complex system.

In terms of predicting bioaccumulation, the modeling approach in AQUATOX is more complex than generally applied in Projects of this type. So I suppose the description of bioaccumulation is "theoretically rigorous". Several alternatives to the description of bioaccumulation for lower food web organisms are offered in Section II.

5. What supporting data are required for the calibration/validation of the model on the spatial and temporal scales necessary to address the principal need for the model (as defined above)? What supporting data are required to achieve the necessary level of process resolution in the model?

A tabulation of the full data requirements for modeling transport, fate, and bioaccumulation of PCBs will be developed.

6. Based upon your technical judgment, are the available data, together with the data proposed to be obtained by EPA, adequate for the development of a model that would meet the above referenced purposes? If not, what additional data should be obtained for these purposes?

The available data, and data collection planned by EPA, are generally consistent with the information required to develop the PCB transport, fate, and bioaccumulation models. There is not an abundance of data for PCBs in the water column or biota, however, and there appear to be some problems with the quality of dissolved PCB measurements. Several other specific weaknesses are evident:

- *Data to support empirical state variable linkages - The model linkages for solids and organic carbon states depend upon many observations from which correlations must be constructed. From what I have seen (scatter plots of all TSS and TOC data), the data may not be available to support this approach.*
- *Loading data*
- *Partition coefficients*
- *Diet data*
- *Spatial and seasonal variability of PCB concentrations in plankton and benthos*

II. SPECIFIC COMMENTS ON MODELING FRAMEWORK DOCUMENT

Modeling Framework Document

MFD should make better use of long-term data when developing the conceptual model and identifying important processes: examples from 20-year record? Request GE YOY fish PCB data and 1979-80 sediment PCB data. Analysis of long-term data is helpful to determine whether PCB dynamics are controlled by internal (sediment inventory) vs. external (loadings, events) factors. This exclusion from the MFD is unfortunate.

Aquatic Biological Conceptual Model description is good; quite complete treatment for lower trophic levels.

Lack of specification of model grid and process selection/representation are weaknesses of the MFD.

Sediment Mixing and Diffusion Processes

In all reviews of sediment mixing processes I have seen, bioturbation is primarily attributed to the activities of benthic invertebrates. Benthic feeding by fish is mentioned by several authors as a possible mixing mechanism, but the extent and intensity of this factor over time is highly uncertain. Attempting to relate sediment mixing to observed carp feeding is tenuous at best. In fact I suspect that the cause of bioturbation really doesn't matter, as in any case the process is parameterized in the models as the depth of the surficial mixed layer, "background" resuspension, and lumped pore water diffusion. Some additional consideration should be given to the 15 cm mixed depth: what is the rationale for this value? Can it be independently confirmed?

On the other hand, there appear to be inconsistencies in the MFD and the model documentation, regarding how molecular diffusion, bioturbation, and groundwater infiltration/percolation are represented in the transport/fate models. Are these modeled as distinct processes, or are they limped into a single transport term?

Spatial Domain of PCB Transport and Fate Models

Given the opportunity, modelers will always attempt to include contaminant sources within the modeling spatial domain. Modeling the sources improves the accuracy of the mass balance and the consistency of the model. It is terribly frustrating to see an otherwise good model compromised by uncertainty in the specification of loadings. In this case, extending the spatial domain of PCB transport and fate models appears valuable, in terms of both calibration/model testing, and ability to address modeling objectives.

I sense that an unstated objective of the MFD is to deal with remedial alternatives and forecasts of

PCB concentrations in the rest-of-river (confluence to Woods Pond) as conceptually distinct from the remediation of the upper river. I foresee numerous problems resulting from this subdivision of a system in which there is active communication of PCBs downstream. Hopefully, this can be addressed at the Public Meeting.

The spatial domain of the model as conceptualized ("rest-of-river") will not address the effect of remedial actions taken above the river confluence, in terms of reducing the upstream loadings of PCBs compared to loadings measured during the 1999-2000 period. Remedial actions are underway in the ½ mile upstream reach adjacent to the GE site, and are planned for the next 1 ½ mile reach. If effective, these remedial actions should substantially reduce upstream PCB loadings. Thus, the loadings used for model calibration will be different than loadings used for predicting future conditions, even for "no action" scenarios. The MFD report does not address how the magnitude of the PCB loading reductions due to remedial actions upstream will be determined. If the modeling domain included the ½ -mile and 1 ½ -mile reaches, then the PCB loading reductions resulting from remedial actions could be simulated by modifying sediment PCB concentrations in the remediated areas. It seems obvious that doing this would strengthen the utility of the models in terms of the stated modeling objectives.

If extension of the modeling domain upstream is not done, then the methods for estimating the effectiveness of upstream remediation should be described in the MFD. Or is the assumption being made that remediation will eliminate upstream PCB loads entirely? Perhaps I do not understand how the "relative risk" paradigm is being applied to the modeling results?

Sediment PCB Data Analysis and Use in Models

What is most striking to me about the maps of PCB distribution in soil and sediment, are the high concentrations (and presumably mass) of PCBs in the river banks. Given what I presume to be this enormous inventory of PCBs in direct proximity to the river, I wonder whether bank erosion might not represent a worse-case scenario for PCB transport and exposure. As I understand it, erosion and slumping of the river bank cannot be resolved or represented in the sediment transport model? Some consideration should be given to how such an event could be simulated.

Aggregation of sediment PCB data should be based on :

- organic carbon normalization;
- deposition regime of sampling location;
- as well as river mile and grain size factors, which were discussed.

The methodology for determining initial conditions for PCB sediment concentrations in 1979, for the hindcast verification, should be discussed. The first sediment PCB measurements were made in 1979-80. Are these data comparable to current measurements, in terms of sampling resolution and analytical methods? If not, won't bias in specification of initial conditions for the hindcast be a problem for long-term validation?

PCB Partitioning

Use of Kp, when you mean Koc, is a pain. Greater consistency would improve the document. The prevalent usage of PCB data normalized to dry weight in sediment is inconsistent with the models, which are representing partitioning to organic carbon/matter.

Inconsistencies in the partitioning data presented in the MFD strongly suggest that additional data be collected to support calibration of PCB partition coefficients in water (including seasonality & range of POC values) and sediment.

The following are two tables with some selected values for PCB partition coefficients in sediment and water. These could be greatly expanded, if desired. The point is that by comparing the range of these values to partition coefficients measured in the Housatonic River, some judgements can be made regarding their quality and representativeness.

PCB partition coefficients measured in sediment

literature source	log K_d	log K_{poc}	log K_{doc}
Di Toro et al. (ES&T, 1985)	5.1	6.6 (cites range of field data as 4.2 - 6)	
Hunchak-Kariouk et al. (ES&T, 1997)		4.6	4.7 - 5.6
Brownawell and Farrington (Geochimica..., 1986)	3 - 4.4		
Velleux and Endicott (JGLR, 1994)		6.35	5.35
QEA (Hudson River, 1999)		5.6 (reversibly sorbed PCBs)	

PCB partition coefficients measured in water column

literature source	log K_d	log K_{poc}	log K_{doc}
Eadie et al. (Chemosphere, 1990)		5.8	3.9
Velleux and Endicott (JGLR, 1994)		6.35	4.35
QEA (Hudson River, 1999)		5.6 - 6.3	

Regarding the low values of sediment Kp, I intended to look at the range of partition coefficients obtained using a 3-phase (dissolved/POC/DOC) partitioning calculation, but then I ran out of time.

The issue of whether phase separation of sediment samples has been done by filtration or centrifugation remains. The response to Peer Review comments says:

> Most of the samples were centrifuged to collect the pore water, a procedure recognized as leaving organic material in the suspended phase.

However, this conflicts with the memos provided from Rich DiNitto, which indicate that filtration predominated. Help!

Spatial Resolution of Models

The spatial segmentation of the water column in AQUATOX appears reasonable, but the same segmentation applied to the surficial sediment bed may be too coarse. Cursory examination of the sediment PCB distribution maps, indicates that concentrations deviate in a systematic manner between mid-channel and near-shore regimes, longitudinally within subreaches, and with depth and location within Woods Pond. This suggests that additional sediment segmentation may be warranted. The relationship between erosion and deposition regimes as predicted by sediment transport model, and the AQUATOX sediment segmentation should also be considered. If not, then AQUATOX may erroneously associate low (or high) PCB concentrations with sediments being resuspended from a particular EFDM sediment segment.

Calibration and Verification of AQUATOX

Considerable effort is required to calibrate partitioning, particle transport, and especially bioaccumulation processes in a PCB transport and fate model. The parameterization and empirical relationships used to estimate parameter values, as presented in the AQUATOX documentation, should be viewed as prior estimates which are then updated through the calibration process. “Little calibration will be necessary for ecosystem variables in AQUATOX" conflicts with my own experience. Models of PCB transport and fate, and underlying theory, are not sufficiently robust that parameter vaulues determined *a priori* can account for all of the site-specific variability that is observed in critical model parameters. This is not a weakness of AQUATOX specifically, rather an acknowlegement that all transport and fate models are imperfect representations of chemical behavior in an extremely complex system.

I am concerned that calibration and validation of bioaccumulation predictions in AQUATOX depend primarily upon predictions of PCB concentrations at the top of the food chain:

> The final confirmation will be in the ability to simulate the observed PCB concentrations in the key fish species.
>
> The test of the validity of this approach will be how effects from the lower food web are integrated into the predicted fish concentrations, for which there is a substantial data set.

This may leave important aspects of the bioaccumulation predictions at lower trophic levels untested and unconstrained, including those which resolve sediment versus water column contaminant exposure and tropic accumulation pathways. I would prefer that calibration and validation consider predictions at all trophic levels to be important, as this would better constrain the model.

Statements that little calibration will be necessary in either WP or upstream river reaches seems unlikely. River systems impacted by in-place pollutants are challenging at the least, as demonstrated by efforts to model PCB dynamics in the upper Hudson River and the Fox River.

Tandem application of AQUATOX and EFDM is not presented in QAPP Section 4.8. Specific comparisons (QAPP, 4.7.1) are not defined: what spatial and temporal resolution; how will data be aggregated? What is the objective of this comparison?

AQUATOX ecosystem model

The "classical" or conventional approach to modeling chemical bioaccumulation in food chains and food webs (as defined by Weinenger, Nordstrom, Thomman, Connolly, Gobas, to name a few), is based on a mass balance applied at the whole-organism level. Mass balance equations for representatives of each trophic level are coupled in a prescribed manner by the specification of predator-prey relationships. These can be simple or complex, including such factors as change in diet with age, season, and/or location. It can be demonstrated, either by observation or via sensitivity analysis, that bioaccumulation of highly-hydrophobic chemicals is very sensitive to predator-prey relationships. This is especially true for organisms consuming a diet including both benthic and pelagic food items, because of the large gradient in hydrophobic chemical exposure observed between water and sediment.

The accuracy and fidelity of the predator-prey specification is constrained by the data available to describe organism diet, typically gut content analyses. This approach of specifying predator-prey relationships can be criticized for (at least) the following:

- Gut content data reflect the predator-prey relationship at a particular time and place. Depending on the circumstances, this data may be extremely variable. Collecting this data is labor-intensive and logistically difficult; therefore, even in the best case, there is usually not enough gut content data to adequately define the predator-prey relationship in a continuous manner. Although other analytical methods (nitrogen isotope ratios, for example) may overcome some of the discontinuity problem, the general problem of uncertainty in this specification of predator-prey relationships remains.
- Gut content data reflect the predator-prey relationship at the time of sampling, and have no predictive (forecasting) power other than assuming that tomorrow will be like today. We know this not to be true, therefore bioaccumulation forecasts made with specified predator-prey relationships will be inherently uncertain.

Several food web models have been developed which couple the bioaccumulation process with ecosystem simulation of predator-prey dynamics. AQUATOX, BASS, and the Mercury Cycling Model are examples of this type. The ecosystem model is used to simulate the density and/or biomass of food web organisms. The density of different organisms serves to modify the specified prey preference of predators according to abundance. The goal of this approach is to develop food web models which overcome both of the limitations identified above, (namely) the use of insufficient, discontinuous measurements to specify predator-prey relationships, and the lack of forecasting ability. Unfortunately, there are a number of problems with this approach as well:

- A great deal of site-specific data are required to properly constrain an ecosystem simulation, much more than will exist for an aquatic ecosystem unless great resources are brought to bear;
- Many fish, especially top predators, may have specific prey preferences and are essentially insensitive to prey abundance;
- Unless confirmed by gut contents data (the need for which was supposed to be avoided), ecosystem simulation of predator-prey relationships may be no more (and possibly less) accurate than use of gut contents data to directly specify predator-prey relationships;
- Especially worrisome is the possibility that an unconstrained ecosystem simulation could shift the modeled predator-prey relationship towards an unrealistic feeding scenario, for example a planktivorous fish feeding on detritus or benthos due to the relative abundance of biomass. An error of this sort apparently occurred in the AQUATOX application to PCBs in Lake Ontario (Park, August 1999), when parameterization error caused amphipod biomass to drop below the minimum level for feeding by smelt. This error in the ecosystem simulation had an effect on PCB bioaccumulation which cascaded up through the trophic levels.
- I am aware of no research to demonstrate that bioaccumulation predictions made by ecosystem-based food web models are more accurate and/or reliable than specified food web models;

- The forecasting ability of ecosystem-based food web models depends upon whether the forcing functions (climate, nutrient and energy fluxes, fisheries management, invasive species, ...) can be anticipated. Since this is not likely, the best that can be done is to use the ecosystem model for bounding analysis, something that can probably be done directly using life history data for the food web organisms of interest.

QEA has commented that AQUATOX ecosystem dynamics (biomass change with time) will be unconstrained by data. They argue it is better to specify diet based upon site data and literature, and deal with uncertainty in the diet specifications. The Peer Review Panel lacks an ecological modeler. I know I am not, so I really cannot evaluate whether the planned collection of biomass data will adequately constrain the simulation of ecosystem dynamics in AQUATOX. AQUATOX calibration/validation (QAPP 4.7) <u>does</u> include biomass as a calibration goal.

If population densities of trophic levels modeled in the AQUATOX food web cannot be confirmed by available biomass data, trophic linkages based upon both abundance and prey preferences will be unconstrained in the absence of site-specific diet studies. The ecosystem dynamics incorporated in AQUATOX are otherwise irrelevant for the Housatonic River application. The uncertainty in bioaccumulation predictions (including pelagic vs. benthic contaminant accumulation routes) may be large (to an unknown extent), especially over annual and longer time scales. It is crucial for bioaccumulation modeling that the trophic linkages be realistic during simulation; an ecosystem modeling approach doesn't appear to guarantee this. The conventional engineering modeling approach may be less uncertain.

The model must do better than "produce realistic ecosystem dynamics based on general principles", it must do the best job possible to describe the predator-prey relationships in the ecosystem.

To sum this up, there may be little to gain by using the ecosystem-based modeling approach in the Housatonic River. For this application, it adds unnecessary complexity to an already difficult modeling problem. It also specifies the collection of biomass data which is irrelevant to the problem at hand. These aspects are distractions from the stated modeling objectives. Ecosystem model simulation has no direct utility in the context of the modeling objectives; it is only relevant in terms of establishing trophic (predator/prey) relationships. My recommendation is that the ecosystem dynamics simulated by AQUATOX be constrained so that predator-prey interactions in the food web remain consistent with applicable site-specific gut content studies, and that data should be collected to validate the trophic pathways in the food web model.

> Labor-intensive gut analyses and studies of depth of disturbance over seasons was clearly beyond the scope of this site investigation.

I tend to question this, given the extent of soil and sediment sampling performed for this study.

Statement that general feeding preferences “work well” in defining predator-prey relationships (4.7.2) is not necessarily true. Lake Ontario AQUATOX application as an example. Site data on gut contents and calibration are necessary, in the experience of most modelers.

AQUATOX Model Description

AQUATOX mass balance equations account for contaminant transfer associated with deposition and erosion, but apparently not pore water diffusion nor groundwater infiltration. Is this correct? These may be significant processes for sediment-water contaminant exchange under low flow conditions.Similarly, AQUATOX does not account for accumulation of DOC in sediment pore water as a result of detrital carbon decomposition. This differs from several other diagenesis models I have reviewed, where detrital carbon undergoes transformation to DOC as well as CO_2.

Are inorganic solids (D1, D2 and D3) treated as state variables in AQUATOX? Do they adsorb PCBs? Is this based on assuming an organic carbon content?

AQUATOX makes use of a variety of chemical parameter correlations based upon the octanol-water partition coefficient (equations 49-54, 69-70, 72, 75, 78, 82). These correlations are commonly used to generalize laboratory or field observations of hydrophobic organic chemical parameters, usually under specific controlled or site-specific conditions. As such, they are an acceptable means of generating initial (prior) estimates of chemical parameters for transport, fate and bioaccumulation models. However, adjustment of these estimates is usually necessary as part of the model calibration process; if the data available for validation is suitably constraining, adjustment is almost inevitable. It is not clear from the model description whether AQUATOX allows ready calibration of these parameters, or whether such calibration is anticipated by the modeling team.

A whole literature exists of correlations for K_{oc} (KOM in equations 49 and 50). For the sake of consistency, it would be worth considering results from studies where K_{oc} was determined simultaneously for both particulate and dissolved organic carbon phases, such as Eadie et al. (Chemosphere, 1990).

Regarding the use of Swackhamer et al.’s kinetic model for phytoplankton bioaccumulation, it would be worthwhile to update AQUATOX to reflect the use of organic carbon as the sorbing matrix instead of lipid (Skoglund and Swackhamer, ES&T, 1999). Also, the exposure time and growth rate parameters in that model should be coupled to the relevant variables in AQUATOX. Of course, the phytoplankton BAF predictions must themselves be validated to data.

I am not sure why AQUATOX calculates non-equlibrium partition coefficients for invertebrates (eqn. 53) and fish (eqn. 54). Is this done to address slow biphasic chemical elimination? Otherwise, it seems to make AQUATOX inconsistent with other bioaccumulation models for invertebrates (Morrison, Landrum) and fish (Gobas, Thomann). Why not calculate equilibrium partition coefficients from organism lipid content?

Morrison's steady-state model should be considered for modeling invertebrates; it appears to do about the best job in matching the BAFs and BSAFs observed for PCB congeners.

AQUATOX incorporates a kinetic model for sediment partitioning, as opposed to the equilibrium partitioning model used in most contaminant transport and fate models. The limitations of the equilibrium partitioning assumption for modeling hydrophobic organic chemicals have been discussed *ad nauseum*, yet the assumption remains popular for a number of reasons. First, it greatly simplifies and speeds the solution of the mass continuity equations in the model. Second, it requires only the measurement of "standard" water quality measurements for parameterization. And third, it appears to work pretty well in real systems. The kinetic model used in AQUATOX is Karickhoff's reversible 2-compartment model. This model, and the rate parameters cited in the documentation, was developed from gas purge reactor experiments conducted with hexachlorobenzene (HCB) and several other less-hydrophobic chemicals. Aside from the possibility of artifacts in these experiments (gas purge reactors are complex because air-water and sediment-water partitioning of chemical occurs simultaneously), HCB may be a poor model for PCBs, based on differences observed in partition coefficients for these two chemical classes. A whole succession of researchers have questioned the generality of this model (I'll get the references), including whether it is any better than simple equilibrium partitioning (or simple modifications to equilibrium partitioning; for example, QEA's Hudson River model). Currently, most process modelers seem to prefer distributed parameter or heterogeneous radial diffusion models. Incorporation of such kinetic models is well beyond the capabilities of AQUATOX, as it requires high spatial and temporal resolution, treatment of sediment hysteresis, and solution of stiff partial differential equations.

I need to spend more time with Equation 82. What data is this relationship based upon? There should be much more data available to test this relationship. Doesn't AQUATOX use a better calculation of respiration rate (species-specific bioenergetic) than the allometric cited from Thomann? Also, I will have to check whether this seems to fit for invertebrate respiration rates.

<u>EDFC Model Description</u>

Process representation for PCB transport/fate in EFDC are overly-simplistic, both in relation to state-of-art and representations in AQUATOX. Simple EFDC process representations seems inappropriate, for example lack of 3-phase partitioning.

EDFC calibration/validation will include comparisons to long-term sediment accumulation rates, although WP predictions will likely be low biased due to absence of primary production.

<u>Modeling Framework: EFDC (Abiotic) vs. AQUATOX (Biotic) Components</u>

There is no such thing as biotic and abiotic PCBs. This creeps into the description of EDFC, for example:

EFDC will model abiotic components and AQUATOX will model both biotic and abiotic components.

This code modification will allow, for example, the capability to define seasonal and spatial differences in the organic carbon fraction of each solids class to account for winter-summer differences in phytoplantkon that are included as a component of field measurements of grain size distributions, TSS and POC. Specific modeling of volatilization and microbial degradation in EFDC is not envisioned other than as lumped first-order rates.

This separation is not as clean a separation of processes as , for example, transport/fate vs. bioaccumulation. Using separate programs to model abiotic and biotic transport and fate processes is untested; success of this approach has not been demonstrated.

Separation of biotic and abiotic components of PCB transport and fate is a potentially significant weakness. This separation is artificial, and appears to be motivated by the selection of models that are not truly appropriate for this application. Alternatives:

- Model all PCB transport/fate in EDFC (But can it model eutrophication and toxics simultaneously? What about hardpan/gradient preserving sediment bed simulation?) Or other water quality model (IPX?);
- Model all PCB bioaccumulation in AQUATOX or other food web bioaccumulation model;
- Choose an alternative model which can simulate both biotic and abiotic processes;
- Invest effort to develop such a model (based, for example, on EFDC); this effort would probably be less than that proposed for handling complex linkages in the MFD.

It seems likely that EFDC and AQUATOX predictions of water and sediment concentrations will diverge. This will result from differences in spatial/temporal resolution, and from differences in the transport/fate processes (and their formulation) included in each simulation. It is extremely important to understand both the magnitude of divergence in predictions and their underlying causes. Therefore, total PCBs should be state variables modeled by both EFDC and AQUATOX.

Since only selected congeners will be simulated, AQUATOX will not simulate total PCBs and the results generated by AQUATOX will not be compared to field observations of total PCBs.

I think it is very important that both EFDC and AQUATOX model total PCBs as a state variable. Note the importance of verifying constant congener distribution; if distribution varies, chemical parameters for total PCB will not be constant:

- Loading history: Aroclors 1254 and 1260

- Dehalogenation of congeners in Woods pond sediment (similar to preblems in Hudson River TIP)

  The data are being evaluated to determine the dominant congeners using a variety of procedures, including Euclidian distance and principal component analyses, to determine the degree of homogeneity of the congener distributions, as well the changes in congener distributions over time and space. The results of these analyses for the sediment and water samples will be used to estimate the congener distributions in other samples where only Aroclors were measured, and similarly to the output of modeled components where only total PCBs are being tracked.

OK, but will these statistical approaches give good, quantitative results?

Another issue to consider is the methodology for long-term validation:

> Following calibration of the models using data from 1991-2000, the models will then be validated by assigning initial conditions based on data sets collected during 1979-1980. Model validation will be based on a long-term simulation beginning in 1979 and ending in 1990. The long-term simulation from 1979-1990 is intended to provide validation of the models with an independent data set. Continuation of the validation period of the simulation through 1991-2000 then provides an additional rigorous test of the predictive capability of the models using a continuous simulation against data available within a 20-year period. If the models can successfully reproduce the observed data sets over a 20-year period, then the credibility of the model for projecting the potential impacts of alternative remedial action scenarios >50 year decadal time scales will be greatly enhanced.

A reasonable approach. One question about this: What is the contingency plan in the event that the long-term hindcast fails to validate the models? How and where will corrective action take place?

Model Framework Linkages

State variable linkages for solids/sorbents between models are complex procedures (models, in effect): grain size vs. organic/inorganic, BOD vs. POC... These procedures must themselves be calibrated. Is the empirical approach for establishing linkages good enough to use in a quantitative modeling framework? Seems like this has not been addressed, yet it may be significant in overall uncertainty of modeling.

"Linked" state variables (example: organic carbon sorbents) must be calibrated/confirmed like other predicted state variables. Intricacy of linkages may lead to a great deal of effort and potential for errors.

While the description of EFDM-AQUATOX linkages in the QAPP(4.9.3) refers to erosion and deposition fluxes, in fact it is vertical particle velocities which are linked (?).

A related concern is how deposition and resuspension velocities are aggregated in both space and time (QAPP 4.9.3.6). In particular, it is not clear how the aggregation scheme will handle erosion and deposition occurring within the same averaging period and/or aggregated segment. Will the individual (gross) deposition and resuspension velocities be averaged separately for transfer to AQUATOX, or will net particle velocity (deposition - resuspension) be averaged/transferred? This detail of the aggregation and linkage schemes must be properly designed to ensure that the correct interaction of sediment and suspended solids in AQUATOX.

The model linkages between solids and organic carbon sorbent state variables, are a potential weakness of the modeling framework design, and potentially a significant source of error. While these linkages do solve the problem of incompatible state variable definitions between models, there are a number of problems which are not adequately addressed in the MFD:

- Several of the linkages may not conserve mass
- Several of the linkages are based on empirical relationships, which may be only weakly predictive

The key requirement for the model linkage is the necessity to maintain a careful mass balance of flow and constituent loads between HSPF, EFDC and AQUATOX.

<u>Data linkages from EFDC to AQUATOX</u>

Equations 4-3 and 4-4: How good are the spatially- and temporally-dependent estimates of TOC:TSS? Don't you really want the POC:TSS ratios?

Equation 4-3: Shouldn't the TOC:TSS ratios be different for each PIM size class?

PIM export/import: From this I assume that AQUATOX must partition PCBs onto PIM? I could not confirm this from the documentation. How are these partition coefficients determined, since by definition these particles have no organic carbon content?

POM deposition/resuspension: Cohesive solids deposition and resuspension velocities are applicable to the POM associated with fine-grained cohesive solids; they would not for phytoplankton (unless river phyto are much smaller than diatoms). Is POM a state variable independent of phytoplankton? Again, this is something I could not confirm in the AQUATOX documentation

Data linkages from HSPF to AQUATOX

Equations 4-8 and 4-9: Is there an error in these equations (what happened to BOD)? From the mingling of model state variables and data I cannot tell, but I suspect these linkages do not conserve mass. If so, doesn't this violate an objective of the MFD? Regardless, POC and DOC boundary conditions must be calibrated and validated as predicted states.

Model Uncertainty Analysis

Model uncertainty should be addressed by a combination of:

- Monte Carlo analysis; preliminary, similar to sensitivity analysis (AQUATOX description makes use of too few realizations to be quantitative)
- Bayesian Monte Carlo; informative parameter distributions based on calibration (may be computationally intensive for dynamic simulations)
- Alternative bounding calibrations (although this approach can be abused by subjective application)

Particle Transport

It is not clear how the resuspension data provided in the Gailani et al. (September 2000) report will be used to generate the spatially-distributed resuspension properties required to model the sediment bed of the river and pond. The report points out that considerable variation of sediment bulk properties and erosion rates were observed above Woods Pond, and that further effort would be required to develop a sediment mapping of these properties and test them with a sediment transport model. How well this is done may determine the success or failure of the sediment transport simulation.

HSPF Simulation of Loadings

Is the HSPF modeling approach and/or site data adequate to model PCB watershed loadings?

HSPF has not been used to simulate PCB fate and transport in watersheds....

Complete and accurate solids/sorbents and PCB upstream loadings are critical. The target tolerances for HSPF predicted PCB concentrations and loadings is +- 50 % (Table 4-4, QAPP); if loadings are off by a factor of 2, how can the transport/fate predictions of PCB chemical concentration be more accurate (tolerance of 50 % over long term)? Is there sufficient data to estimate loadings by conventional approaches? Request confluence data: discharge, TSS, POC, dissolved and total PCBs. Not a lot of data (7 storms + 15 monthly values) but will look at the possibilities.

Request confluence data: discharge, TSS, POC, dissolved and total PCBs. Not a lot of data (7 storms + 15 monthly values) but will look at the possibilities.

HSPF in-stream water quality calibration is not an objective (QAPP 4.5.9) because HSPF is being used to calculate and deliver nonpoint loadings to other models; but isn't HSPF used to calculate upstream ("source reach") boundary conditions for solids and PCBs? Isn't this the largest component of external solids and PCB loadings? If so, then it seems calibration of HSPF boundary conditions should be a major objective. What about PCB and solids loads from the West branch of River?

HSPF linkage to EDFC requires translation of TSS into particle size classes; how much data will be available to do this? Will it be treated as a function of flow or hydrograph stage?

HSPF is being used to model the boundary condition for PCBs at the confluence, therefore it incorporates PCB loadings from the river reaches under/planned for remediation. How will HSPF simulations be modified to reflect loading reduction due to remediation? Or, will the modelers assume all PCB loads at the confluence to be zero in forecast simulations?

> ... to account for the effects of upstream removal actions for the purposes of modeling no action and other remedial alternatives, one can hypothesize various boundary fluxes ranging from a zero input condition to some minimal background PCB loading for the model forecast.

To perform the hindcast validation, continuous PCB loads must be estimated for the 1979-1999 period. How will HSPF be applied over this period? I would expect the contaminant potency factors POTFW and POTFS to decline over long time scales, following the cessation of PCB usage and discharge. If this is true, then the initial conditions in HSPF must be determined by independent observations or estimates analogous to the for initial conditions for PCB concentrations in river sediments. If not, then I question whether HSPF is a realistic model for simulating nonpoint PCB loadings.

Need for Additional Data

Add to key PCB parameters: phyto/zooplankton BAF (phyto and zoo sampled together with dissolved water), benthos BSAF (invertebrates sampled together with sediment), dietary chemical assimilation, sediment feeding selectivity, invertebrate uptake and elimination rates (and respiration coupling). Suggest not considering or calibrating bioaccumulation model for biotransformation, unless specific congeners known to be metabolized are modeled.